231. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part X. Saturated Aliphatic Acids.*

By J. F. J. Dippy.

The thermodynamic dissociation constants of ten saturated aliphatic acids have been accurately determined. These acids consist of the *n*-series extending from *n*-butyric to *n*-nonoic acid, and the branched-chain *iso*butyric, diethylacetic, *iso*valeric, and trimethylacetic acids. The constants recorded hitherto had been (with one exception) the result of less dependable work and were expressed in classical terms; consequently, there was serious lack of agreement and doubt existed as to the order of strengths. It is now found that the dissociation constants of the *n*-acids (excluding *n*-butyric acid) tend to fall as the series is ascended, which is in accordance with expectation. Methylethylacetic, diethylacetic, and *iso*valeric acids are comparable with *n*-butyric acid, however, in possessing abnormally high strengths; this phenomenon is discussed. *iso*Butyric acid does not differ from propionic acid in strength despite the marked fall in trimethylacetic acid; this observation may be related to the anomalous order found in the *p*-alkylbenzoic acids (J., 1937, 1774).

Importance can be attached to relatively small differences in the dissociation constants of acids only if the available values are thoroughly reliable and strictly comparable. Accurate knowledge of the strengths of saturated aliphatic monobasic acids has hitherto been confined to acetic, propionic, and *n*-butyric acids. A number of earlier investigators published classical constants, determined conductometrically, for the *n*-series as far as *n*-octoic acid, but these figures were mostly conflicting (see Table IV), and no theoretical conclusions could safely be based on the evidence. Moreover, as this series is ascended the solubility in water diminishes rapidly, and measurements on two given acids might involve series of solutions differing widely in concentration, thus rendering invalid a comparison of K_{class} values.

Attention has been drawn to the possibility that differing heat capacity and entropy effects might have a significant influence upon the apparent relative strengths of acids (Hammett, *J. Chem. Physics*, 1936, **4**, 613; Baker, J., 1937, 1775), but the author's answer to this objection (*ibid.*, p. 1776) justifies the actual use made here of dissociation constants in theoretical organic discussion. The criticism may actually be put to test. It is recognised that these imputed complications are reflected in the data for acetic, propionic, and *n*-butyric acids, and yet the relative order is indisputable, no matter whether the values relate to a fixed temperature or to θ (temperature of maximum *K*, *i.e.*, K_m; see Harned and Embree, *J. Amer. Chem. Soc.*, 1934, **56**, 1050), as will be seen from the following dissociation constants (Harned and Ellers, *ibid.*, 1933, **55**, 652, 2379; Harned and Sutherland, *ibid.*, 1934, **56**, 2039).

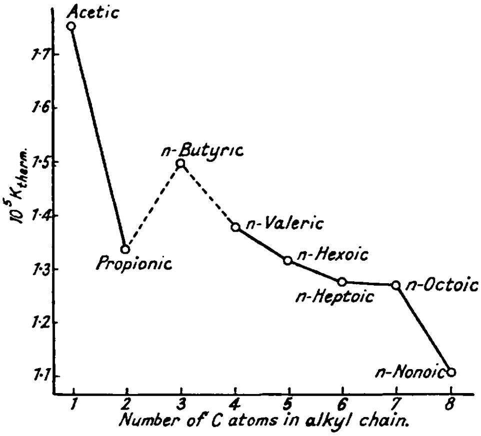
Acid.	$K_{10°}$.	$K_{25°}$.	K_m.
Acetic	1·729	1·754	1·76
Propionic	1·326	1·336	1·34
n-Butyric	1·576	1·515	1·57

The mean thermodynamic dissociation constants ($10^5K_{\text{therm.}}$) obtained in the present investigation are contained in Table I, and those for *n*-acids are shown graphically in the figure. The constants for acetic and propionic acids, due to Dippy and Williams (J., 1934, 1888) and Harned and Ehlers (*loc. cit.*), respectively, are also included. Measurements on acids higher than *n*-nonoic acid cannot be made in water because of their negligibly small solubilities.

TABLE I.

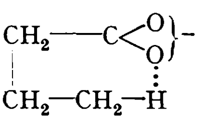
Acetic acid	$1{\cdot}75_5$	*iso*Butyric acid	$1{\cdot}38$	*n*-Hexoic acid	$1{\cdot}32$
Propionic acid	$1{\cdot}33_5$	Trimethylacetic acid	$0{\cdot}891$	*n*-Heptoic acid	$1{\cdot}28$
n-Butyric acid	$1{\cdot}50$	*iso*Valeric acid	$1{\cdot}67$	*n*-Octoic acid	$1{\cdot}27_5$
n-Valeric acid	$1{\cdot}38$	Diethylacetic acid	$1{\cdot}77_5$	*n*-Nonoic acid	$1{\cdot}11$

The order, acetic >*n*-butyric>propionic, was already known, and now it can also be said that the constants of the higher *n*-acids fall in gradual sequence to *n*-octoic acid, although in nonoic acid a marked further decrease is observed; the low constant obtained for this acid is confirmed by Franke (*Z. physikal. Chem.*, 1895, **16**, 477), who records *1·12.*[*]



Except for *n*-butyric and *n*-nonoic acids, it is seen that extension of the alkyl group has a distinct effect which increases very gradually with growth of the chain, and this is in harmony with our present knowledge of the inductive effect (+ *I*) of alkyl in such combination (*e.g.*, Kharasch and Flenner, *J. Amer. Chem. Soc.*, 1932, **54**, 674). Evans and Gordon (private communication), in a study of alkaline hydrolysis of the esters of the present acids, also find that the energies of activation rise with lengthening of the chain, as necessitated by an increasing inductive effect.

It would appear on this evidence that *n*-butyric acid has an unexpectedly high dissociation constant. This has already been pointed out by Bennett and Mosses (J., 1930, 2364), who contrast this acid with propionic acid on the one hand and heptoic acid on the other; reference to *n*-valeric acid in place of the latter acid may now confidently be made, so increasing the validity of the observation. These authors suggest that in *n*-butyric acid, as also in *o*-toluic acid, the diffuse positive outer field, which they associate with methyl, directly affects carboxyl in such a way as to facilitate ionisation. In both systems the methyl and carboxyl groups are taken to be in close proximity in space, although in the fatty acid, approach of the groups is intermittent on account of rotation of the chain, and consequently enhancement of strength is less marked. A somewhat different interpretation of the abnormal strength of *o*-toluic acid has been advanced by Dippy, Evans, Gordon, Lewis, and Watson (J., 1937, 1421; cf. Baker, this vol., p. 445), and an explanation of the strength of *n*-butyric acid along similar lines may be suggested. On this view, high acid strength may be attributed to the reluctance of the anion to recombine with hydrion in the reverse reaction of the ionisation equilibrium, as a result of a process of the annexed type. The electronic rearrangement suggested in the *o*-toluic system is, of course, impossible in the aliphatic acid, so that the suggestion is more tentative here; nevertheless, it must be borne in mind that the oxygen which associates itself with hydrogen actually bears a negative charge. The possibility of steric hindrance of the geometrical type cannot, of course, be excluded, but it is rendered less likely by the absence of abnormality in β-phenylpropionic acid (see phenyl-substituted acids, J., 1937, 1008).



$$\begin{array}{l} CH_2\text{——}C\left<\begin{matrix}O\\O\end{matrix}\right\}- \\ \;\vdots \qquad\qquad\qquad \vdots \\ CH_2\text{—}CH_2\text{—}H \end{array}$$

In connexion with the foregoing anomaly of *n*-butyric acid, it should be noted that Harned and Sutherland (*loc. cit.*) find a maximum dissociation constant at 8°, whereas for acetic and propionic acid θ lies between 20° and 25°, as indeed do the values of θ for the other organic acids (K, 10^{-5} to 10^{-4}) so far studied. Thus it becomes evident again

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[*] Classical constants from the literature are employed merely as confirmatory evidence, and are distinguished by italics. All constants, thermodynamic and classical, are in terms of 10^5K.

that *n*-butyric acid is inconsistent, and that some influence, not common to the other acids, is profoundly affecting the heat of ionisation of this acid. Examination of other physical properties, *e.g.*, molecular volume, does not reveal any unusual behaviour on the part of *n*-butyric acid, and this is to be expected if the foregoing explanation is correct, involving, as it does, a disturbance affecting the anion.

Since *iso*valeric and diethylacetic acids also possess a 3-carbon alkyl chain, their dissociation constants should also be unusually high (cf. Bennett and Mosses, *loc. cit.*); the results in Table I fulfil this expectation (compare also Billizer's value of *1·68* for methylethylacetic acid; *Monatsh.*, 1899, **20**, 666). On the basis of inductive effects alone, the order of strengths should be *n*-butyric$>$*iso*valeric$>$diethylacetic acid, whereas the converse is true. Chain-branching might account for this order, if the suggested chelation occurs, in view of the more frequent approach of the terminal groups to carboxyl in these cases.

The operation of the foregoing effect cannot be traced in the available data for the unsaturated aliphatic acids (Ives, Linstead, and Riley, J., 1933, 561), doubtless because here it will be masked by the additional polar factors introduced by the vinyl group which are very potent (cf. Dippy and Lewis, J., 1937, 1008).

It might be contended that examination of the figure indicates that, if propionic acid is excluded, the remaining acids show a gradual fall of *K* from acetic acid onwards. It is not possible to see, however, what factor interferes solely in propionic acid; even the marked effect which Baker and Nathan (J., 1935, 1844) associate with alkylation of methyl in a conjugate system is more likely to produce the order acetic$<$propionic. One cannot escape the conclusion, therefore, that the abnormal member of the homologous series is *n*-butyric acid. Further, if it is considered that hydrogen of methylene (γ-position) is also capable of participating in a chelation process, and this assumption is certainly permissible (cf. Evans, J., 1936, 785), the strengths of the homologues above *n*-butyric acid must also reflect an enhancing influence. On inspection of the figure it becomes apparent that, if *all* the points representing the acids above propionic acid were displaced downward, a perfectly continuous diminution of strength from acetic acid would be revealed.

The effects of chain-branching in acids other than those compared above with *n*-butyric acid are also significant; it is found that introduction of a single methyl group into propionic acid at the α-carbon atom (giving *iso*butyric acid) fails to bring about a fall in strength (the marked *increase* in strength shown by earlier data is not verified), and yet the substitution of two methyl groups (*i.e.*, in trimethylacetic acid) brings about a normal diminution. It is also indicated that there is no perceptible change in *K* on passing from *n*-valeric to β-methylvaleric acid, Franke's constant of *1·4* being taken as the most acceptable for the latter (cf. p. 1227). Moreover, these observations are consistent with those of Evans and Gordon (private communication) on the hydrolysis of the corresponding esters. This failure of the single methyl group to reduce *K* when substituted in propionic acid is doubtless connected with the presence initially of a methyl group in the acid, since acids of the type $CH_2X{\cdot}CO_2H$ (where X is some substituent other than methyl) all suffer a roughly proportionate fall in strength when methyl is introduced into the α-position; this is seen by comparing the data in the following two lines:

$CH_2Ph{\cdot}CO_2H$, *5·03*[1] $CH_2(OH){\cdot}CO_2H$, *15*[2] $CH_2Cl{\cdot}CO_2H$, *155*[2]
$CHMePh{\cdot}CO_2H$, *4·25*[2] $CHMe(OH){\cdot}CO_2H$, *13·8*[2] $CHMeCl{\cdot}CO_2H$, *146·5*[3]

[1] Dippy and Williams, *loc. cit.* [2] Ostwald, *Z. physikal. Chem.*, 1889, **3**, 369. [3] Lichty, *Annalen*, 1901, **319**, 380.

There has already been reason to infer that methyl, in certain circumstances, may fail to exert, through the molecule, its normal influence of repelling electrons. It was pointed out by Dippy and Page (this vol., p. 357) that sometimes substitution of methyl in hydroxyl causes an *increase* in acid strength, and to the instances already cited may be added the comparison of the strengths of glycollic and methoxyacetic acid (*15* and *33·5* respectively; Ostwald, *loc. cit.*; cf. Böeseken and Kalshoven, *Rec. Trav. chim.*, 1918, **37**, 131, and Palomaa, *Centr.*, 1912, ii, 596); examination of other evidence also goes to show that this reversal of the normal polar effect is characteristic of the methyl of the methoxyl group. The origin of the inductive effect of alkyl is obscure and, indeed, it seems now to be still more probable that it is determined largely by the mode of combination of the group (see Ingold, *Chem. Reviews*, 1934, **15**, 238).

The unusual strength of *iso*butyric acid is not a disconnected observation. There is a striking analogy between the order of strengths of *p*-ethyl-, *p*-*iso*propyl-, and *p*-*tert.*-butyl-benzoic acids (K 4·43$_5$, 4·43, and 3·98, respectively; Baker, Dippy, and Page, J., 1937, 1774) and that of the comparable propionic, *iso*butyric, and trimethylacetic acids (K 1·33$_5$, 1·38, and 0·891, respectively). Moreover, the systems are much alike; the aromatic differs from the aliphatic only in that the benzene nucleus intervenes between the carboxyl and the alkyl group, and there is every reason to suppose that effects arising from the latter will be transmitted readily in both systems. It seems very likely, therefore, that in these aliphatic acids a " partial inversion " of the polar effects of Et, Pr^{β}, and Bu^{γ} is again being observed. Both Baker and Nathan's explanation (*loc. cit.*; J., 1937, 1775) and the author's alternative suggestion (*ibid.*, p. 1776) are capable of accounting for this order.

The relative strengths of the methylamines may also be connected with the foregoing observation. Harned and Owen (*J. Amer. Chem. Soc.*, 1930, **52**, 5079) record the following reliable data (10^5K_b), NH_3, 1·79; NH_2Me, 43·8; $NHMe_2$, 52·0; NMe_3, 5·45. It is unlikely that bulk effects account for this anomalous order, especially in view of recent indications that the angle for the C–N–C bonds in trimethylamine approximates to 108° (Brockway and Jenkins, *ibid.*, 1936, **58**, 2036). Thus if polar factors are responsible exclusively, it would appear that an increasing restraint is being put on the inductive effect of methyl as methylation of ammonia progresses.

EXPERIMENTAL.

Materials.—The acids were obtained from Schering–Kahlbaum, except trimethylacetic acid, which was kindly provided by Dr. D. P. Evans, who prepared it by a Grignard synthesis. Purification of the liquids was effected by fractional distillation, and, where possible, by subsequent partial crystallisation (in a freezing mixture) and draining of residual liquid. Satisfactory equivalents were obtained throughout on titration with baryta water. The corrected b. p.'s (and m. p.'s) of the fractions employed in conductivity measurements are recorded below. These constants compare favourably with the best values in the literature for the synthetic acids.

Acid.	B. p. (M. p.).	Acid.	B. p. (M. p.).
n-Butyric	162—162·5°/768·8 mm.	*n*-Nonoic	M. p. 15°
n-Valeric	99·5—100/23 mm.	*iso*Butyric	78/34 mm. (153·5/756 mm.)
n-Hexoic	M. p. −0·5	Diethylacetic	92·5—94/13 mm.
n-Heptoic	124—125·5/18 mm.	*iso*Valeric	99·5/37 mm. (175/756 mm.)
n-Octoic	M. p. 17·5	Trimethylacetic	M. p. 35

Measurements.—The conductivity measurements were made on aqueous solutions at 25° as already described (Parts I—III and V). The shunt method of measuring cell resistance was eliminated altogether (even for conductivity water) by incorporating in the bridge low-inductance decade resistance units of 100,000 ohms and 1 megohm. The accurate determination of the conductivity of the most dilute solutions was facilitated by the use of a variable air condenser (maximum capacity 0·001 microfarad) in parallel with the resistance arm containing the decade boxes; in this way the balance points became more distinct, although the actual settings were not altered.

The water employed in the preparation of the acid and salt solutions had a conductivity of 0·9—1·0 gemmho. The initial acid solutions were made up to 250 ml. at 25°, except for the more sparingly soluble heptoic and octoic acids where 500 ml. of solution were prepared.

Table II summarises the observations made on the ten acids; in each case one complete run is given in detail (the method of calculating thermodynamic constants has been described before).

The values of Λ_0 (acid) (Table III) were computed from the measurements made on aqueous solutions of the sodium salts by the method outlined in Parts I—III.

In passing from acetic to *n*-butyric acid the anion mobility (l_a) falls from 40·9 to 35·1, a decrease of about 6 units, but on proceeding further through the series the fall in l_a becomes less marked; when the ion comprises as many as nine carbon atoms the value

TABLE II.

Normal series.

n-*Butyric acid.*

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1351	11·73	13·59	1·52	$1{\cdot}47_5$
	5·406	19·73	(1·50)	(1·46)
	4·142	22·69	1·53	$1{\cdot}49_5$
0·07285	3·388	24·94	1·52	1·49
	2·941	26·67	$1{\cdot}51_5$	$1{\cdot}48_5$

10 Determinations :
limits of $10^5K_{therm.} = 1{\cdot}47_5$—1·53.

n-*Valeric acid.*

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1338	14·11	12·02	$1{\cdot}43_5$	1·39
	13·96	12·01	1·42	$1{\cdot}37_5$
	6·636	17·26	1·41	1·37
0·07214	4·189	21·71	$1{\cdot}42_5$	1·39
	4·048	22·03	1·42	$1{\cdot}38_5$
	3·326	24·10	$1{\cdot}40_5$	$1{\cdot}37_5$

11 Determinations :
limits of $10^5K_{therm.}$ = 1·36—$1{\cdot}39_5$.

n-*Hexoic acid.*

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1347	12·70	12·15	1·34	$1{\cdot}29_5$
	6·179	17·37	1·35	$1{\cdot}31_5$
	5·754	17·86	1·33	$1{\cdot}29_5$
0·07259	3·553	22·76	1·35	1·32
	2·832	24·97	$(1{\cdot}30_5)$	$(1{\cdot}27_5)$

9 Determinations :
limits of $10^5K_{therm.} = 1{\cdot}29_5$—$1{\cdot}34_5$.

n-*Heptoic acid.*

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1338	5·267	18·38	1·30	1·27
	4·537	19·82	1·31	1·28
0·07214	3·796	21·49	$1{\cdot}29_5$	$1{\cdot}26_5$
	2·718	25·24	1·29	1·27
	2·206	28·05	$1{\cdot}30_5$	$1{\cdot}28_5$

9 Determinations :
limits of $10^5K_{therm.}$ = 1·27—$1{\cdot}29_5$.

n-*Octoic acid.*

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1338	1·522	33·32	$1{\cdot}29_5$	1·27
	0·9232	42·43	$1{\cdot}30_5$	$1{\cdot}28_5$
	0·8042	44·94	$1{\cdot}28_5$	1·27
0·07314	0·7738	46·08	$1{\cdot}30_5$	$1{\cdot}28_5$
	0·5446	53·88	$1{\cdot}28_5$	1·27

8 Determinations :
limits of $10^5K_{therm.}$ = 1·27—$1{\cdot}28_5$.

n-*Nonoic acid.*

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1338	0·9515	38·07	1·08	$(1{\cdot}06_5)$
	0·6295	47·53	$1{\cdot}14_5$	1·13
	0·5151	51·33	$1{\cdot}10_5$	1·09
0·07214	0·4357	56·04	$1{\cdot}13_5$	$1{\cdot}11_5$
	0·3903	58·16	1·10	1·09

9 Determinations :
limits of $10^5K_{therm.}$ = 1·09—1·13.

Branched-chain series.

iso*Butyric acid.*

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1339	10·12	14·24	$1{\cdot}41_5$	1·38
	3·082	25·02	1·40	$1{\cdot}37_5$
	2·201	29·52	1·41	$1{\cdot}38_5$
0·07244	2·149	29·84	1·41	1·38
	1·025	42·50	$1{\cdot}41_5$	$1{\cdot}39_5$

12 Determinations :
limits of $10^5K_{therm.}$ = 1·37—$1{\cdot}39_5$.

Diethylacetic acid.

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1338	7·469	18·27	1·81	$1{\cdot}75_5$
	3·520	26·40	$1{\cdot}82_5$	1·78
	2·720	29·47	$(1{\cdot}77_5)$	(1·73)
0·07214	2·052	34·21	$1{\cdot}82_5$	$1{\cdot}78_5$
	1·501	39·54	1·81	$1{\cdot}77_5$
	1·199	43·52	$(1{\cdot}78_5)$	$1{\cdot}75_5$

10 Determinations :
limits of $10^5K_{therm.} = 1{\cdot}75_5$—1·79.

iso*Valeric acid.*

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1347	12·40	13·96	$1{\cdot}71_5$	$1{\cdot}66_5$
	6·095	19·60	1·69	1·65
	4·502	22·81	$1{\cdot}70_5$	$1{\cdot}66_5$
0·07259	3·229	26·91	1·72	$1{\cdot}68_5$
	2·341	31·49	1·73	$1{\cdot}69_5$

9 Determinations :
limits of $10^5K_{therm.}$ = 1·65—$1{\cdot}69_5$.

Trimethylacetic acid.

Cell const.	10^3C (equiv./l.).	Λ.	$10^5K_{class.}$.	$10^5K_{therm.}$.
0·1338	7·112	13·39	0·909	0·887
	3·642	18·64	0·914	0·895
0·07214	2·704	21·36	0·898	0·881
	1·927	25·32	0·908	0·893

8 Determinations :
limits of $10^5K_{therm.}$ = 0·881—0·902.

of l_a is 27·1. A somewhat similar diminution in ion mobility is found in the cases of acrylic, vinylacetic, and allylacetic acids (Dippy and Lewis, *loc. cit.*; Dippy, *Phil. Mag.*, in the press). As far as the author's observations extend, it can be said that the branching of the alkyl chain reduces the speed of ion migration, so that the order is primary > secondary > tertiary. Thus the isomeric ions arising from *n*-valeric, *iso*valeric, and trimethylacetic acids possess mobilities of 33·4, 32·7, and 31·9 respectively, and a similar conclusion is drawn from the values of l_a in the cases of *n*- and *iso*-butyric and hexoic and diethylacetic acids. The Λ_0 (acid) data recorded by Bredig (*Z. physikal. Chem.*, 1894, **13**, 191), Franke (*loc. cit.*), and Drucker (*Z. physikal. Chem.*, 1905, **52**, 642) show trends comparable with those described above.

The last column of Table III reveals the serious lack of agreement existing between the classical constants published for these aliphatic acids. No fewer than nine constants

TABLE III.

	Mean Λ_0.		Values of $10^5 K_{\text{class.}}$.	
Acid.	Salt.	Acid.[*]	Calculated mean.[†]	From literature.
n-Butyric	85·2	384·8	1·53	1·40,[1] 1·45,[2] 1·47,[3] 1·49,[4] 1·52,[5] 1·53,[6] 1·54,[7] 1·66,[8] 1·75[9]
n-Valeric	83·5	383·1	$1{\cdot}41_5$	1·50,[5] 1·56,[9] 1·6,[4] 1·61[7]
n-Hexoic	80·9	380·5	$1{\cdot}35_5$	1·38,[5] 1·45,[4] 1·46[7]
n-Heptoic	79·3	378·9	1·31	1·31,[5] 1·46[9]
n-Octoic	78·9	378·5	$1{\cdot}29_5$	1·2—1·3,[10] 1·44[5]
n-Nonoic	77·2	376·8	1·12	1·12[5]
*iso*Butyric	84·3	383·9	1·41	1·4,[4] 1·44,[3] 1·45,[11] 1·48,[6] 1·59,[9] 1·62[7]
Diethylacetic	80·5	380·1	$1{\cdot}82_5$	1·87,[3] 1·89,[5] 2·0,[7] 2·03[12]
*iso*Valeric	82·8	382·4	1·71	1·49,[6] 1·67,[5] 1·68,[3] 1·73,[7] 1·79[9]
Trimethylacetic	82·0	381·6	0·909	0·976,[13] 0·978[7]
Acetic (for comparison purposes; Dippy and Williams, *loc. cit.*)	91·0	390·6		

[*] In deriving the Λ_0(acid) values the sodium and hydrogen mobilities of MacInnes, Shedlovsky, and Longsworth (*J. Amer. Chem. Soc.*, 1932, **54**, 2758) were employed, *viz.*, 50·1 and 349·7, respectively.

[†] Mean of $10^5 K_{\text{class.}}$ values determined in this investigation.

[1] Wilsdon and Sidgwick, J., 1913, **103**, 1964.
[2] Bauer, *Z. physikal. Chem.*, 1906, **56**, 215.
[3] Verkade, *Rec. Trav. chim.*, 1916, **35**, 97; 1917, **36**, 197.
[4] Ostwald, *Z. physikal. Chem.*, 1889, **3**, 418.
[5] Franke, *ibid.*, 1895, **16**, 477.
[6] White and Jones, *Amer. Chem. J.*, 1910, **44**, 197.
[7] Billitzer, *Monatsh.*, 1899, **20**, 666.
[8] Kortright, *Amer. Chem. J.*, 1896, **18**, 369.
[9] Drucker, *Z. physikal. Chem.*, 1905, **52**, 642.
[10] Wightman and Jones, *Amer. Chem. J.*, 1911, **46**, 84.
[11] Dalle, *Centr.*, 1902, i, 913.
[12] Walden, *Z. physikal. Chem.*, 1892, **10**, 638.
[13] Pommeranz, *Monatsh.*, 1897, **18**, 575.

were recorded for *n*-butyric acid, the extreme values differing by about 25%. For the most part, the present classical constants are in closer harmony with the lowest figures taken from the literature, although for *n*-valeric and trimethylacetic acids the present values are appreciably lower than any of the earlier ones. Serious doubt has prevailed regarding the strength of *n*-valeric acid, for it will be seen from Table III that two of the four past measurements indicated that it was weaker than *n*-butyric acid, whereas the others showed it to be stronger; it may be that contamination with the stronger *iso*valeric acid accounted for the high results. It is noteworthy that Franke (*loc. cit.*), with two distinct specimens, records constants differing by about 6%, and accepts the lower figure on the ground that it referred to the purer specimen of acid. Since the new figure for this acid is of such theoretical significance, it was decided to secure measurements on different specimens of the acid, but all the runs were in agreement.

The classical constants extracted from the literature are not all of equal merit. In almost every instance the method of successive dilution seems to have been adopted, but the accuracy differs in standard. The quality of the water is rarely mentioned, and on the other hand, an empirical solvent correction has sometimes been applied. Most investigators fail to describe the purity of their acids, a fact which seriously detracts from the value of their measurements. The most extensive investigations were those of Franke, Billizer, and Drucker, and the results which approximate most closely to the present ones are those of the first-named. It is significant that this worker alone consistently stated the purity of his materials; moreover, his results were exceedingly regular and included independent measurements on the sodium salts; his dilution procedure, nevertheless, strictly limited the number of his determinations on the higher acids. Very good agreement with the present results is found with *n*-butyric, *n*-hexoic, *n*-heptoic, *n*-nonoic, and *iso*valeric acids.

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